

HYDROGENATION OF PHENANTHRENE OVER A COMMERCIAL
COBALT MOLYBDENUM SULFIDE CATALYST UNDER SEVERE REACTION CONDITIONS

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Introduction

While it is true that cobalt molybdenum catalysts were developed primarily for the hydrodesulfurization of petroleum residuum streams, they have been applied extensively in laboratory and pilot plant investigations of the production of quality synthetic fuels from coal, oil shale and tar sands. In these applications the catalyst has been of interest not just because of its desulfurization capabilities, but also because of its high activity in hydrogenation, stabilization and conversion reactions. The remarkable feature of cobalt molybdenum catalysts is their ability to remain active despite the presence of notorious catalyst poisons, in particular organic sulfur and nitrogen compounds, in the feedstocks undergoing treatment.

Phenanthrene is typical of the hydrocarbons produced during the liquefaction of coal. The staggered phenanthrene-like compounds are thermodynamically more stable (6) than the linear anthracene-like isomers and they are usually present in greater abundance in coal derived liquids (e.g. 1). Partially hydrogenated derivatives of phenanthrene are very active hydrogen donors in coal extraction. In one study 9, 10-dihydrophenanthrene was reported to be slightly superior to tetralin in hydrogen donor activity (2). Perhydrophenanthrene was much less active, and the possibility of over hydrogenating the solvent in a hydrogen donor coal liquefaction scheme is widely recognized. The extent to which phenanthrene is hydrogenated in a catalytic solvent hydrogenation reactor is therefore of considerable interest.

In addition some conversion to lower molecular weight species (hydrocracking) is usually desirable. While cobalt molybdenum is much less active in this regard as compared with catalysts containing an acidic component, it has proven superior in terms of hydrocracking selectivity in at least one instance. Gardner and Hutchinson found cobalt molybdenum to be active and selective for hydrocracking polyphenyls including biphenyl (4). Catalysts on acidic supports were less selective and produced mostly coke. Penninger and Slotboom observed substantial quantities of 2-ethylbiphenyl and biphenyl in the reaction products from the thermal high pressure hydrogenolysis of phenanthrene indicating that hydrogenation and α -ring-opening at the 9, 10-position was in fact taking place (7). The product distribution from cracking over nonacidic or low acidity catalysts frequently resembles that obtained in thermal cracking processes. Since cobalt molybdenum catalysts are known to be selective in the hydrocracking of biphenyl, and it might be speculated that biphenyls can be formed from phenanthrene over cobalt molybdenum in a manner similar to that observed in thermal cracking, it was hoped that some cracking at the central ring of phenanthrene might be accomplished. This speculation was a major driving force behind the present investigation. The economic advantages of hydrocracking at the inner rings of condensed ring aromatics as compared with terminal ring cleavage are readily apparent in terms of reduced hydrogen consumption, higher yields and in some cases higher quality products.

It was evident from the very beginning of this investigation that much higher temperatures than normally encountered in packed bed reactors would be required in order to obtain substantial yields of cracked products. Catalyst

deactivation due to carbon formation on the catalyst surface would likely be a problem. However, liquid fluidized beds have been employed on a commercial scale in the hydrodesulfurization of petroleum residuum streams (H-Oil) and on the pilot plant scale in the liquefaction of coal (H-Coal). One of the advantages of the liquid fluidized bed reactor is that provisions can be made for the continuous addition and withdrawal of catalyst. The addition of fresh catalyst could conceivably overcome the deactivation problem when operating at high severity.

Experimental

The catalyst employed in this investigation was supplied by the Nalco Chemical Company and carries the designation Nalco-471. According to the manufacturer's specifications the catalyst consists of 12.5% MoO_3 and 3.5% CoO supported on an alumina base. The surface area and total pore volume are 295 m^2/gm and 0.55 cc/gm respectively. High purity hydrogen (99.995% according to the supplier's specifications) was obtained from the Matheson Gas Products Company in 3500 psig cylinders. Phenanthrene, 98% purity, melting point 99-101°C was purchased from the Aldrich Chemical Company. An elemental analysis of the phenanthrene (Galbraith Laboratories, Knoxville, TN) indicated that the sample consisted of Carbon: 93.69%, Hydrogen: 5.48%, Nitrogen: 0.01%, Sulfur: 0.42%, and Oxygen: 0.39% by weight.

The reactor, Figure 1, is a steady flow type constructed of a 1/2 inch heavy wall (0.083 inch) Type 316 stainless steel tube and heated by a Marshall tubular furnace, model 1016. The reactor charges approximately five grams of catalyst. Thermocouples were inserted about 1/2 inch into both ends of the catalyst bed, and a preheat zone of glass chips was provided at the bed inlet. Liquid phenanthrene was metered into the reactor by a precision Ruska proportioning pump, model 2252-BI, with a heated barrel. Various discharge rates from 2 cc/hr to 240 cc/hr could be obtained by selecting the proper choice of gear ratios. The hydrogen flowrate was monitored by a flow meter constructed of a 29 inch length of 0.009 inch I.D. capillary tubing and a Barton model 200 differential pressure cell. The capillary pressure and reactor pressure were controlled respectively by a Tescom pressure regulator, model 26-1023-002 and a Tescom back pressure regulator model 26-1723-24. Flow rates were controlled with a Hoke Milli-Mite needle valve. Liquid products were collected in two high pressure accumulators constructed of one inch schedule 80 stainless steel pipe and Swagelok butt weld connectors. Product gases were vented through a low pressure accumulator in dry ice-propanol, through a wet test meter, and collected in a polyethylene gas bag.

The catalyst was crushed and sieved to 20/30 mesh and calcined at 1000°F in air for four hours. After calcining the catalyst was charged to the reactor and the system pressure tested with hydrogen. Presulfiding was carried out at 250 psig using a hydrogen sulfide (2%) - hydrogen (98%) mixture. During presulfiding the gas flow was set at 5 l/hr/gm catalyst and the reactor temperature was maintained at 400°F for 5 hours. After this period the temperature was raised at a rate of 2°F/min to 600°F and held for 1 hour. Then with sulfiding gas flowing at a minimal rate the reactor was cooled to room temperature.

The phenanthrene feed was spiked with elemental sulfur to a total sulfur content of 1.0% by weight. During startup the spiked feed was cut in with the hydrogen sulfide-hydrogen mixture flowing at 1000 psig and 500°F. Once liquid product was detected in the high pressure accumulator the gas mixture was replaced with pure hydrogen and the reactor was brought to operating conditions. After a period of time sufficient for three displacements of the reactor volume the reaction products were directed to a second high pressure accumulator and a yield period begun. At the termination of a yield period the liquid product was collected and stored in a freezer, and the gas product was immediately analyzed.

The system was brought to a new set of run conditions and the procedure repeated. During all adjustments care was taken to assure that the rate of temperature rise never exceeded 120°F/hr and that the catalyst was at all times in contact with sulfur.

The products were analyzed on a gas chromatograph which utilized a hydrogen flame ionization detector and possessed temperature programming capabilities. The column for the liquid product analysis was packed with 5% SE-30 on 60/80 mesh Chromosorb P, AW. The gas analysis column was packed with Chromosorb 102. The identification of the various product peaks was accomplished by measuring the retention time of pure compounds and by a GC-mass spectral analysis. The former method was used to identify most of the lower molecular weight hydrocarbons and the latter method was relied upon for identification of many of the high molecular weight peaks. The mass spectra of some of the more important product peaks are presented in Figure 2. Additional information on the analytical methods used in this investigation is available in masters theses by Huang (5) and Early (3).

Results

A total of eighteen yield periods were successfully completed in two series of experiments. The operating conditions and product yields are presented in Tables 1 and 2, respectively. These yields have been adjusted to meet a 100% carbon material balance. Before discussing these results it must be pointed out that problems were encountered in two areas.

Because of the large heat effect it was not possible in some instances to operate the reactor isothermally. In the most extreme case the temperature difference between top and bottom of the reactor was of the order of 90°F. Thus the reported temperatures at the milder operating conditions must be considered nominal values only. (The reported temperature is the numerical average of the reactor top and bottom temperatures.) In nonadiabatic-nonisothermal reactors it is not uncommon that the temperature at some point within the reactor will exceed either the top or bottom temperature. Such a phenomenon would go undetected in our experimental set-up since thermocouples were only located at the bed inlet and exit. The actual upper and lower temperatures are presented in Table 1.

The second problem was encountered in the analytical portion of the investigation. Three peaks on the chromatogram were found to be mixtures of two components. The unresolved pairs were: 1. asym-Octahydrophenanthrene isomer and n-Butylnaphthalene, 2. Perhydrophenanthrene isomer and n-Butyltetralin and 3. Octahydrophenanthrene isomer and Dihydrophenanthrene. The unresolved "component" yield known to consist of asym-Octahydrophenanthrene and n-Butyltetralin is plotted as a function of temperature (pressure, space velocity constant) in Figure 3. The curve exhibits two maxima. Thermodynamics considerations suggest that the high temperature maximum is due principally to n-Butylnaphthalene; whereas, the low temperature maximum is due principally to Octahydrophenanthrene. The mass spectra of this unresolved peak from products of the 750°F run and the 800°F run are consistent with this contention. The dotted line in Figure 10 is an estimate of the magnitude of each individual contribution to the unresolved peak drawn in such a manner that the sum of the individual component estimates is equal to the total. Similar estimates were made for the other unresolved pairs (5). Separation of the unresolved components in this manner is admittedly speculative and qualitative. Nevertheless this procedure does provide a simplification which is consistent with the observed data and aids greatly in the qualitative interpretation of the data.

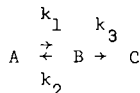
Since rapid deactivation of the catalyst was expected, especially at the more severe operating conditions, it was necessary to maintain a record of declining catalyst activity. This was done by repeating the selected base conditions, of 850°F, 2000 psi, and 2.0 gm/hr/gm in the first set of experiments and 600°F,

2000 psi, 2.0 gm/hr/gm in the second. While no significant deactivation was observed in the second set of experiments (WH-09), Figure 4 shows that both the conversion of phenanthrene and the conversion to C_{13} decreased with respect to grams of oil on catalyst in the first set of experiments (WH-08). As expected, the sharpest decline in catalyst activity was observed when the more severe operating conditions (1000°F, 1500-2500 psi) were examined.

Yields of the various hydrogenation products of phenanthrene are presented in Table 2 and Figure 5. Large quantities of octahydrophenanthrene and perhydrophenanthrene isomers were observed in many of the products. (The various isomers are lumped together in the figures). At 2000 psig and a space velocity of 2 gm/hr/gm, octahydrophenanthrenes are produced in 82% yield at 600°F. With increasing temperatures the octahydrophenanthrenes are further hydrogenated to perhydrophenanthrenes until a maximum yield of approximately 62% perhydrophenanthrenes is reached at 750°F. Beyond this temperature the yield of perhydrophenanthrenes decreases as the thermodynamic equilibrium is shifted to favor the less saturated species. Cracking reactions are also a factor at the elevated temperatures as illustrated in Figures 6, 7, and 8. The presence of n-butyldecalin and decalin in the products indicates that some cracking of perhydrophenanthrene is taking place. However it appears that at the temperatures required to hydrocrack perhydrophenanthrene (at 2 gm/hr/gm and 2000 psig) the equilibrium is shifted away from perhydrophenanthrene formation. No evidence of large branched paraffins that might be anticipated from mechanisms involving ring opening of perhydrophenanthrene were uncovered in the mass spectral analyses. Large quantities of tetralins and naphthalenes were observed in the cracked products. The presence of large quantities of n-butane and n-butyl substituted tetralin, naphthalene and decalin indicates that the major reaction paths involve saturation and cleavage of terminal rings. In Figure 9 various grouped product yields at 950°F and 2000 psig are plotted versus space time. Again it is evident that the formation of two ring compounds precedes the formation of one ring compounds.

The only evidence of cracking at the central ring was the presence of trace quantities (less than 1 mole % yield) of biphenyl and cyclohexylbenzene in some of the reaction products. Slightly higher yields of 2-ethylbiphenyl were obtained. The maximum occurred at about 900°F (WH-08-02) and corresponded to the maximum in dihydrophenanthrene yield. It should be pointed out that these data do not entirely dispel the possibility of cracking at the central ring. It would be interesting to conduct some experimentation in the same temperature range but at much lower pressures than employed in the present investigation where the equilibrium yields of dihydrophenanthrene would be higher. Of course catalyst deactivation would likely be even more serious a problem than encountered in the present study.

Because of the near isothermal behavior of the high temperature runs it is possible to perform a crude analysis of the reaction kinetics. A simple model which appears to describe our system is:



where A represents phenanthrene, B represents hydrogenated product and C represents cracked products (C_{13}). If it is assumed that the equilibrium reaction is rapid in comparison with the cracking reaction, then one can show that the overall conversion of phenanthrene to cracked products should follow first order kinetics (5). But before a meaningful analysis of the data can be undertaken it is necessary that the rate constants be corrected for the observed decline in catalyst activity.

This was done by defining the activity as the ratio of the observed first order rate constant to the first order rate constant obtained by extrapolating the deactivation plot, Figure 4, to zero grams of oil on catalyst. The activity was then calculated for each yield period using the deactivation curve of Figure 4. A plot of $\ln(1-x)$ versus $a(\text{activity}) \times \tau(\text{space velocity})$, Figure 10, confirms that the hydrocracking reaction is indeed correlated with first order kinetics. The activation energy was calculated to be 40 kcal/gmole. Comparison of his value with an activation energy of 65 kcal/gmole estimated from Penninger Slotboom's thermal data (7) indicates that some catalysis of the cracking reactions is operative.

ACKNOWLEDGEMENTS

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REFERENCES

1. Aczel, T., Rev. Anal. Chem. 1, 226 (1972).
2. Curran, G.P., Struck, R.T. and Gorin, E., I&EC, Proc. Des. Dev. 6, 166 (1967).
3. Early, W.F. II, Master of Science thesis, University of Mississippi, May, 1976.
4. Gardner, L.E. and Hutchinson, W.M., I&EC Prod. Res. Dev. 3, 28 (1964).
5. Huang, C.S., Master of Science thesis, University of Mississippi, May, 1976.
6. Pauling, L., The Nature of the Chemical Bond, 3rd Ed., p. 199, Cornell Univ. Press, Ithaca, 1960.
7. Penninger, M.L. and Slotboom, H.W., Erdol und Kohle, Erdgas, Petrochemie 26, 445 (1973).

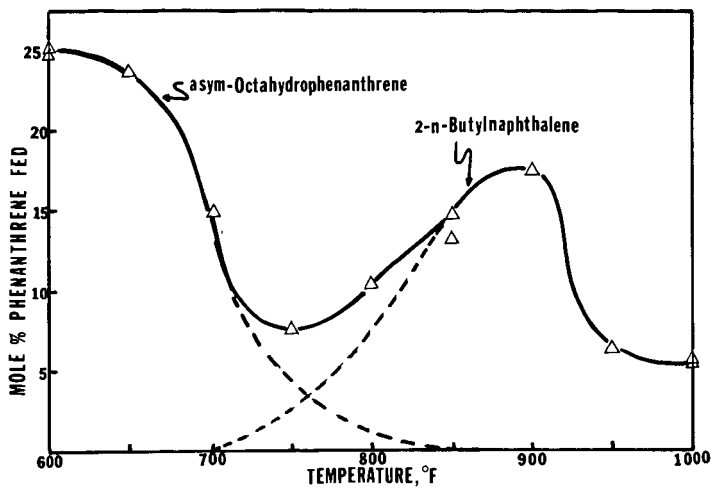


Figure 3 - Yields of Unresolved asym-Octahydrophenanthrene - n-Butylnaphthalene Product Peak.

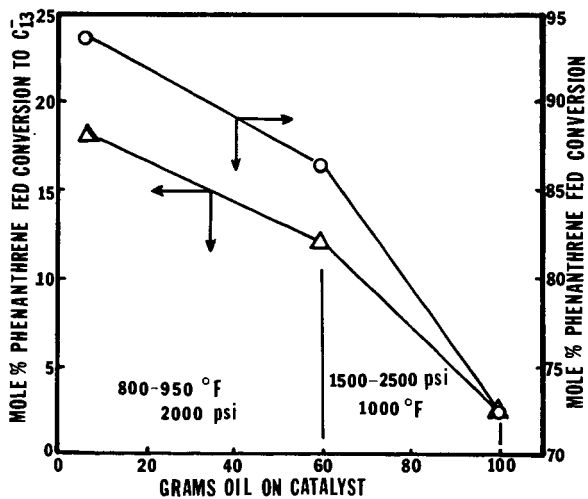


Figure 4 - Conversions at Base Conditions (2000 psig, 850°F, 2 gm/hr/gm).

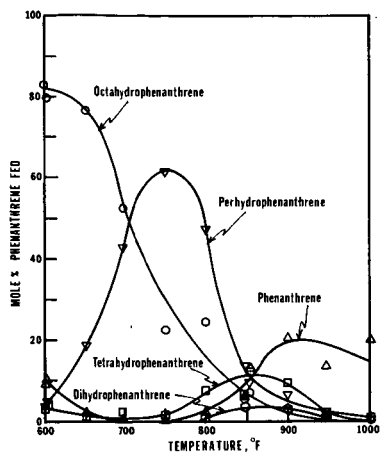


Figure 5 - Yields from the Hydrogenation of Phenanthrene at 2000 psig, 2.0 gm/hr/gm.

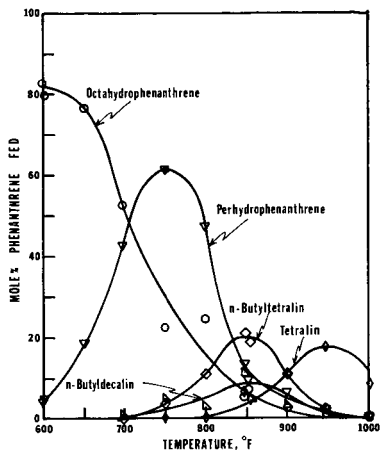


Figure 6 - Yields from the Hydrogenation of Phenanthrene at 2000 psig, 2.0 gm/hr/gm.

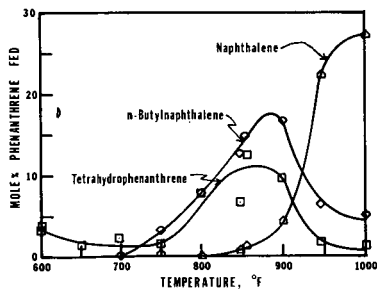


Figure 7 - Yields from the Hydrogenation of Phenanthrene at 2000 psig, 2.0 gm/hr/gm.

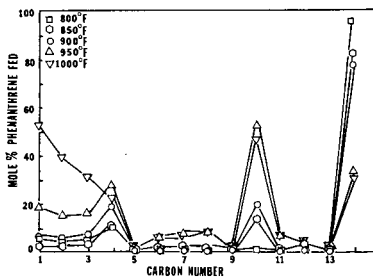


Figure 8 - Product Yields by Carbon Number.

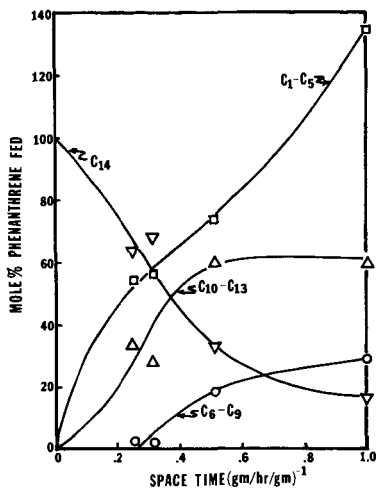


Figure 9 - Product Yields at 2000 psig, 950°F.

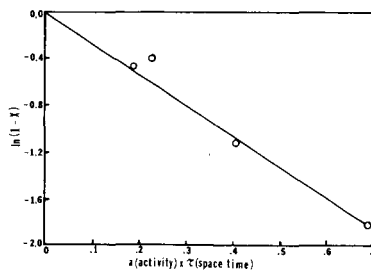


Figure 10 - First Order Plot for Conversion to C₁₃⁻.

TABLE 1

RUN 34-09, HYDROCRACKING OF PHENANTHRENE OVER 5.3566 GRAMS OF SULFIDE
 RUN SUPPLY CO-MC/ALUMINA CATALYST-----NALCOW 471.474-5372.

	1.	2.	3.	4.	5.	6.	7.
YIELD PERIOD NO.	3,000	2,000	1,500	3,000	1,500	2,400	4,000
YIELD PERIOD LENGTH, HRS.	960.9	901.6	811.8	946.8	946.8	945.0	949.5
TOP TEMPERATURE, F	936.0	887.4	788.9	946.8	945.1	945.3	945.1
BOTTOM TEMPERATURE, F	1,023	230.2	180.2	200.2	200.6	200.6	200.6
PRESSURE, PSIG	1,023	230.2	180.2	200.2	200.6	200.6	200.6
LIQUID SPACE VOLUME, CC/HR	1,542	1,933	1,539	1,936	3,897	3,112	0.972
LIQUID SPACE VELOCITY, CM/HR/CM	0.515	0.517	0.516	0.517	0.257	0.251	1.028
SPACE TIME, (CM/HR/CM)*1	15.0	29.5	31.5	17.0	28.5	27.5	12.0
APPROX. H ₂ TREAT RATE, L(STP)/HR	1.5	2.3	2.3	1.9	2.3	2.3	2.3
APPROX. H ₂ TREAT RATE, L(STP)/CM	1.5	2.3	2.3	1.9	2.3	2.3	2.3
CUMULATIVE H ₂ ON CATALYST	3.75	7.90	11.00	19.50	43.75	27.30	32.75
CUMULATIVE GAS OIL/CM CATALYST	7.18	13.93	18.85	33.84	42.78	46.29	52.88
LIQUID MATERIAL BALANCE, WT%	104.6	100.5	101.6	91.7	95.9	97.3	90.4
CATALYST MATERIAL BALANCE, WT%	101.1	104.0	100.3	99.3	99.3	104.3	102.6

FEED CONVERSION, MOLES	91.720	79.398	97.937	86.072	95.578	66.215	94.486
CONVERSION TO C ₁₃ *, MOLES	17.879	22.332	5.244	67.345	91.644	31.560	83.768
HYDROGEN CONSUMPTION, L(STP)/CM	9.688	0.535	0.721	0.581	0.622	0.444	0.805
HYDROGEN CONSUMPTION, WT%	6.188	4.813	5.483	5.222	5.296	3.590	37.235
GAS TO LIQUID (C ₁₃ -C ₁₄), WT%	10.533	95.457	101.300	88.732	95.584	91.307	77.104
C ₁₃ -C ₁₄ YIELD, MOLES	2.960	1.195	0.000	18.134	0.282	0.981	27.032
C ₁₃ -C ₁₄ YIELD, MOLES	19.752	19.150	0.947	40.508	97.343	28.123	61.281
C ₁₃ -C ₁₄ YIELD, MOLES	84.121	77.068	94.756	32.605	4.356	69.040	16.232
SELECTIVITY, %	81.0	85.0	85.0	80.45	80.45	80.45	80.45
SELECTIVITY, %	93.70	89.62	18.06	89.45	104.22	87.99	71.17

*CORRECTED YIELDS BASED ON LIQUID FEED

TABLE 1. (contd.)

RUN NR-08, HYDROGENATION OF PHENANTHRENE OVER 5,3566 GRAMS OF SULFIDE
CO-CATALYST-----NALCO/C 471,474-5372.
RUN SUMMARY

	8.	9.	10.	11.	12.	13.
YIELD PERIOD NO.	3,000	3,000	3,000	3,000	4,000	3,000
TOP TEMPERATURE, HRS.	841.1	1003.4	997.1	1002.7	1003.3	858.3
BOTTOM TEMPERATURE, F	846.0	1000.3	1002.0	998.2	1002.7	844.3
LIQUID FEED RATE, CC/HR	200.2	200.2	190.2	198.3	190.2	200.2
LIQUID SPACE VELOCITY, G/HR/GM	1.939	1.937	1.952	1.945	1.914	1.916
SPACE TIME, (G/HR/GM)-1	0.516	0.516	0.512	0.514	0.523	0.517
APPROX. H ₂ TREAT RATE, L(STP)/HR	16.0	16.0	12.0	20.5	15.5	14.5
INLET GAS RATE, L(STP)/HR	14.0	14.0	10.9	16.4	11.2	10.3
EXIT GAS RATE, L(STP)/HR	11.9	12.1	10.9	16.4	11.2	10.3
CUMULATIVE HRS ON CATALYST	38.00	43.00	50.50	55.33	60.33	67.83
CUMULATIVE GMS CIL/GM CATALYST	55.45	67.46	71.75	79.64	87.02	96.68
LIQUID MATERIAL BALANCE, NTA	90.0	83.1	90.4	87.8	183.7	186.4
CANON MATERIAL BALANCE, NTA	89.9	100.3	99.7	98.0	103.0	104.8

CORRECTED YIELDS BASED ON LIQUID FEED

FEED CONVERSION, MOLES	86.323	79.998	45.904	89.006	74.961	68.178
CONVERSION TO C13-, MOLES	12.230	69.751	30.732	80.144	59.093	2.715
HYDROGEN CONSUMPTION, L(STP)/GM	0.594	0.641	0.319	0.632	0.602	0.313
HYDROGEN CONSUMPTION, NTA	5.140	5.764	2.865	5.893	5.414	2.898
LIQUID YIELD (C9-), NTA	98.882	80.103	90.389	86.941	81.721	101.444
C9-C12 YIELD, MOLES	0.000	18.052	0.911	28.078	7.376	0.270
C9-C12 YIELD, MOLES	8.891	53.353	26.455	68.320	45.371	1.904
C13-C14 YIELD, MOLES	87.770	30.749	69.288	19.856	40.507	97.285
SELECTIVITY, NTA	100.0	100.0	100.0	100.0	100.0	100.0
SELECTIVITY, S2	72.70	76.49	86.98	85.29	77.46	70.11

TABLE 1 (cont'd.)

RUN W-09. HYDROGENATION OF PHENANTHRENE OVER 5.1645 GRAMS OF SULFIDOC
CO-MC/MALLPINA CATALYST-----NALCONC 471, 474-5372.

RUN SUMMARY

	1.	2.	3.	4.	5.
YIELD PERIOD NO.	3,000	3,000	3,000	3,000	3,000
YIELD PERIOD LENGTH, HRS.	616.8	682.8	743.7	791.4	817.3
TOP TEMPERATURE, F	582.8	619.5	652.6	708.0	760.9
BOTTOM TEMPERATURE, F	200.2	200.2	200.2	200.2	200.2
PRESSURE, PSIG	10.2	10.2	10.2	10.2	10.2
LIQUID SPACE VELOCITY, CM/HR/GM	2,010	2,009	2,024	2,011	2,011
SPACE TIME, (CM ³ /HR/GM) ⁻¹	0.498	0.498	0.494	0.497	0.497
APPROX. H ₂ TREAT RATE, L(STP)/HR	13.5	14.8	13.5	13.0	13.0
APPROX. H ₂ TREAT RATE, L(STP)/GP	14.1	15.6	14.5	14.0	14.0
APPROX. H ₂ TREAT RATE, L(STP)/HR	10.8	10.3	10.8	10.8	10.9
CUMULATIVE HRS ON CATALYST	3.18	8.71	13.38	18.18	23.38
CUMULATIVE GMS CIL/GM CATALYST	9.05	17.92	25.88	34.05	42.52
LIQUID MATERIAL BALANCE, WT%	106.2	105.1	109.0	107.3	106.5
CARBON MATERIAL BALANCE, WT%	102.0	100.1	102.3	100.4	100.5

CORRECTED YIELDS BASED ON LIQUID FEED

FEED CONVERSION, MOLES	90.831	97.639	99.492	99.277	99.398
CONVERSION TO C13+, MOLES	1,284	1,258	1,365	1,498	1,001
HYDROGEN CONSUMPTION, L(STP)/GM	0.460	0.554	0.656	0.770	0.456
HYDROGEN CONSUMPTION, WT%	4.1	4.934	5.911	6.911	4.061
LIQUID YIELD, C13+, WT%	0.034	0.043	0.051	0.061	0.034
LIQUID YIELD, C13+, WT%	104.103	104.949	105.889	106.628	104.693
C5-C8 YIELD, MOLES	0.000	0.000	0.000	0.000	0.000
C9-C12 YIELD, MOLES	1.467	1.455	1.580	1.535	1.157
C13-C14 YIELD, MOLES	98.716	98.742	98.635	98.502	98.690
SELECTIVITY, %	114.25	115.60	115.78	101.77	115.63

TABLE 2

RUN W-08. HYDROGENATION OF PHENANTHRENE OVER 5,3566 GRAMS OF SULFIDED
CO-NI/ALUMINA CATALYST-----NALCONO 471,874-5372.

CORRECTED PRODUCT YIELDS BASED ON LIQUID FEED, MOLEN

[illegible]

* MASS SPECTRAL DATA INDICATES THAT THIS PEAK WAS OVERLAPPED BY THE PRECEDING PEAK.

